

Exciton energy transfer in nanotube bundles

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Photoluminescence is commonly used to identify the electronic structure of individual nanotubes. But, nanotubes naturally occur in bundles. Thus, we investigate photoluminescence of nanotube bundles. We show that their complex spectra are simply explained by exciton energy transfer between adjacent tubes, whereby excitation of large gap tubes induces emission from smaller gap ones via Förster interaction between excitons. The consequent relaxation rate is faster than non-radiative recombination, leading to enhanced photoluminescence of acceptor tubes. This fingerprints bundles with different compositions and opens opportunities to optimize them for opto-electronics.

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Carbon nanotubes are rolled graphene sheets [1]. One dimensional quantum confinement makes their band structure fundamentally different from graphene, with sub-bands and singularities in the density of states [1]. These are fully determined by their chiral indexes (n,m), which specify how graphene is folded into each nanotube. Thus, measuring the optical transitions allows in principle to determine the chiral indexes, and fully identify a nanotube sample. For this reason, a massive effort was put to measure photoluminescence in nanotubes since their discovery. However, it took more than ten years to unambiguously detect and identify photoluminescence emission from single wall nanotubes (SWNT)[2, 3]. Indeed, SWNT naturally occur in bundles, due to Van-der-Waals interactions [4], but a significant intensity was only measured when efficient de-bundling was achieved[2, 3]. This paved the way to the interpretation of their complex absorption and emission spectra[2, 3]. The discrepancy between single-particle theory and experiments, pointed to the major role of electron-electron and electron-hole interactions in shaping their band-structure[5, 6]. The exciton binding energies were recently measured[5, 6]. These are very large, from tens meV to 1 eV, depending on diameter, chirality, and dielectric screening [5, 6, 7]. Thus, excitons dominate even at room temperature.

The investigation of the optical properties of nanotubes is now a most pursued research area[2, 3, 5, 6, 7, 8, 9, 10], however this still focuses on individual tubes, in contrast with their natural occurrence in bundles. Furthermore, the luminescence quantum yield of individual SWNTs is very low and this hinders their applications in optoelectronics [3, 9, 10]. Here we present a thorough investigation of absorption and emission spectra of nanotube bundles. We show that their apparently complex spectra can be simply interpreted considering exciton energy transfer between tubes. This is a well known phenomenon in biological systems, conjugated polymers, quantum wires, dots, and other low-dimensional systems[11, 12, 13, 14, 15], which we now clearly identify in nanotubes. We find that energy transfer is a major non-radiative relaxation channel for large

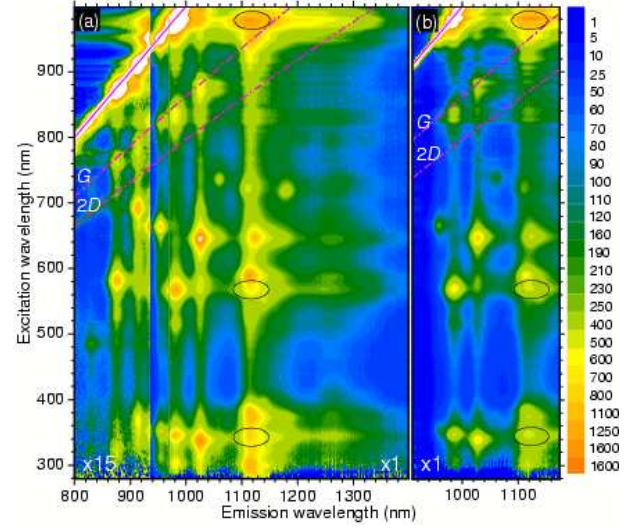


FIG. 1: PLE map for (a) as-prepared suspensions and (b) after two months. Solid lines at upper left corners represent resonances with same excitation and recombination energies. The dashed-dotted lines are associated with G and 2D side-bands. Circles mark emission from (8, 4), (7, 6) and (9, 4) SWNTs, with excitation matching eh_{11} , eh_{22} , eh_{33} of (6, 5).

gap tubes, strongly enhancing the photoluminescence of the acceptor tubes. Thus, contrary to what usually assumed, nanotube bundles could be ideal for high yield optoelectronics applications, far surpassing the poor performance of individual tubes [9, 10]. Furthermore, energy transfer fingerprints bundles with different nanotube concentrations, finally offering a quantitative means to monitor the composition of bundles in solution, a key requirement for research and applications[2, 3].

We measure absorption on CoMoCAT SWNT(South West Nanotechnologies) [16] suspensions in D₂O with sodium dodecylbenzene sulfonate (SDBS) surfactant[2], using a Perkin-Elmer 950 spectrometer. A JY Fluorolog-3 is used for Photoluminescence Excitation (PLE).

Figure 1a plots PLE maps from the as-prepared solution. Each spot can be labeled as $(\lambda_{ex}, \lambda_{em})$, where

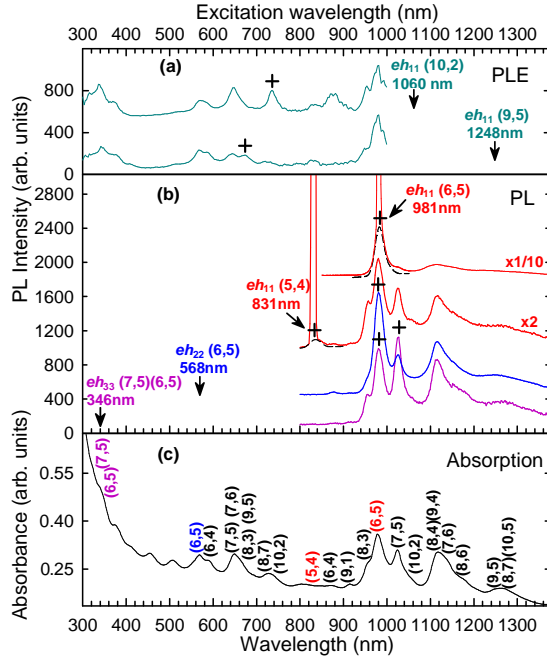


FIG. 3: (a) PLE spectra, (b) emission spectra and (c) absorption spectrum. Arrows indicate detection wavelengths in PLE and excitation in emission. Exciton resonances and associated (n, m) are also shown. Crosses in (a,b) mark exciton-exciton resonances in emission and excitation. Dashed lines in (b) are fits of the (eh_{11} , eh_{11}) resonances. These fits are done after subtracting the fitted Rayleigh peaks of the SWNT solution from that of a D₂O/SDBS solution without SWNTs.

large gap donors is a more efficient way to enhance emission of smaller gap acceptors than the direct eh_{22} and eh_{33} excitation of the acceptors, despite the low photoluminescence quantum efficiency of individual tubes [2].

We can estimate the exciton energy transfer efficiency in bundles as follows. Let us consider the exciton relaxation of two adjacent tubes with different gaps, following the resonant eh_{11} excitation of the larger gap tube. The rate equations of the donor-acceptor system are:

$$\partial n_D / \partial t = G_{pe} - n_D(1/\tau_{nrD} + 1/\tau_{rD}) - n_D/\tau_{DA} \quad (1)$$

$$\partial n_A / \partial t = n_D/\tau_{DA} - n_A(1/\tau_{nrA} + 1/\tau_{rA}) \quad (2)$$

where τ_{DA} is the energy transfer lifetime between donor and acceptor, n_D is the population of excitons in the donor and n_A in the acceptor, τ_{nrD} , τ_{rD} , τ_{nrA} and τ_{rA} are the radiative (r) and non-radiative (nr) lifetimes, G_{pe} the exciton density in the donor created by photo-excitation. An estimation of the EET efficiency is the ratio of acceptor eh_{11} emission intensity ($I_A = n_A/\tau_{rA}$) to that of the donor ($I_D = n_D/\tau_{rD}$). Then, deriving n_A/n_D from Eqs. (1,2) at steady state, we get:

$$I_A/I_D = \frac{1/\tau_{DA}}{1/\tau_{rA} + 1/\tau_{nrA}} \frac{\tau_{rD}}{\tau_{rA}} \quad (3)$$

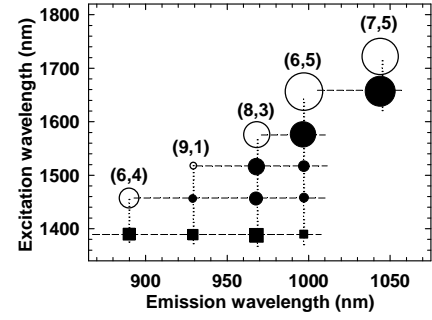


FIG. 4: Some features in the two-photon map of Ref. 6. Open circles: two-photon peaks. Solid circles, squares: EET peaks.

The eh_{11} radiative lifetime is reported ~ 20 - 180 ps, dependent on temperature [27]. For tube diameters ~ 0.75 - 0.95 nm, it is about ~ 20 - 30 ps at room temperature [28]. This is much shorter than the theoretical radiative lifetime (~ 10 ns) [29]. Thus, the observed lifetimes are determined by non-radiative recombination. Eq. (3) can then be simplified as $I_A/I_D \approx \tau_{nrA}/\tau_{DA}$.

We measure a very high I_A/I_D in bundles. E.g., under eh_{11} excitation of the (5, 4) tubes in Fig. 3b, the ratio of photoluminescence intensity of all acceptor tubes with emission above 900 nm [such as (6, 5), (7, 5), (8, 4), (7, 6)] to that at ~ 831 nm of the (5, 4) donor tubes is at least ~ 75 . This indicates that most resonantly-excited (5, 4) eh_{11} excitons transfer their energy to the acceptors, rather than recombine. Thus, in bundles exciton relaxation is comparable or even faster than non-radiative recombination. This fast relaxation suppresses emission from donors. But it significantly increases the acceptors luminescence. This suggests that small bundles entirely formed of semiconducting tubes can be ideal for optoelectronics, such as in light-emitting devices [9, 10].

Two-photon excitation is used to derive exciton binding energies [5, 6]. Fig. 4 summarizes the two-photon map of Ref. 6. The open circles are two-photon exciton resonances. These are slightly shifted with respect to those of Ref. 5 due to the presence of small bundles [6]. Below each two-photon band, Ref. [6] reported a set of peaks, indicated by solid squares and circles in Fig. 4. These appear like a Rydberg series of states, each matching the excitation energy of a larger gap tube, as indicated by horizontal dashed lines in Fig. 4. These are analogous to the energy transfer-induced peaks along each horizontal dashed-dotted line in Fig. 2. We attribute them to emission of small gap tubes due to exciton energy transfer from larger gap tubes in bundles. We assign the four features in Fig. 4 with ~ 1390 nm excitation (solid squares) to EET from (5, 4) donors to (6, 4), (9, 1), (8, 3) and (6, 5) acceptors. Since two-photon luminescence increases quadratically with excitation power, the energy transfer features show more distinct peaks compared to Fig. 1.

In low-dimensional systems, exciton tunneling,

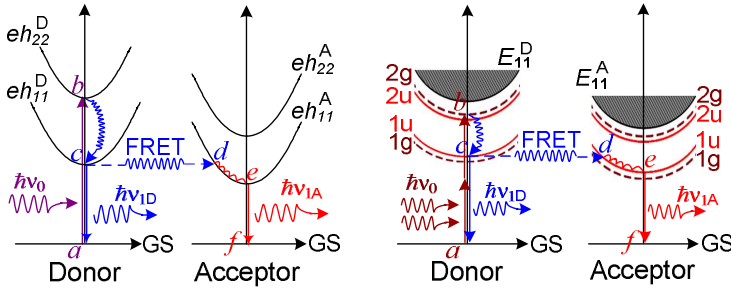


FIG. 5: (Left) Schematic EET from a large gap donor (D) to a small gap acceptor (A). ($a \rightarrow b$) exciton absorption at eh_{22}^D ; ($b \rightarrow c$) fast relaxation to eh_{11}^D within the donor; ($c \rightarrow d$) FRET from donor eh_{11}^D to acceptor exciton states; ($d \rightarrow e$) fast inter-band relaxation down to eh_{11}^A of acceptor; ($e \rightarrow f$) radiative recombination at eh_{11}^A . (Right) Recombination mechanism for two-photon excitation in bundles adapted from Ref.6, where 1g, 1u, 2u and 2g are the even (g) and odd (u) exciton states associated with E_{11} .

photon-exchange and Förster Resonance Energy Transfer (FRET) are efficient exciton energy transfer mechanisms [11, 12, 13, 14, 15, 30]. We attribute energy transfer in bundles to FRET. Indeed, tunneling requires coupling of exciton wavefunctions. Its rate decays rapidly with donor-acceptor distance (R_{DA}) and is very sensitive to the eh_{11} energy difference [30]. The 16 tube species in our experiment have diameters ~ 0.65 - 1.05 nm, $eh_{11} \sim 0.06$ - 0.5 eV, and chiral angle variation ~ 5 - 26° [3, 17]. Therefore, the efficiency should strongly depend on specific donor and acceptor couples. However, the spectrum in Fig. 3b excited at (5, 4) eh_{11} , reproduces the profile of the absorption in Fig. 3c above 850nm, with no (n,m) preference. This suggests that the factor dominating exciton energy transfer in bundles is tube concentration, not symmetry, diameter or bandgap difference, thus exciton tunneling is not the dominant mechanism.

Photon-exchange is exciton-photon coupling with no direct donor-acceptor interaction. It has a smaller dependence on R_{DA} than FRET, thus it can become significant for much longer distances than FRET. However, the lack of significant EET features in isolated tube solutions [3, 17] combined with the low quantum efficiency [2] suggest that even if photon-exchange might exist between bundles or between isolated SWNTs, it is not dominant between adjacent tubes in a given bundle.

FRET is a very efficient exciton energy transfer mechanism via a resonant, near-field, dipole-dipole interaction [11, 12, 13, 14, 15]. It is commonly observed in biological systems, conjugated polymers, wires, dots [11, 12, 13, 14, 15], where it dominates at short and intermediate distances (0.5-10nm) [11, 12, 13, 14, 15]. Its efficiency is determined by the spectral overlap of donor emission and acceptor absorption, by R_{DA} , and by the relative orientation of emission and absorption

dipoles [11]. The rate of energy transfer is proportional to R_{DA}^{-6} [11]. The FRET efficiency in bundles is expected to be high. Indeed, there is a large overlap between emission of large gap tubes and absorption of small gap tubes. SWNTs in bundles are parallel, giving a maximum dipole orientation factor. They aggregate with small wall-to-wall distance [4, 21]. This makes higher multipolar contributions possible as well [11, 12]. Indeed, considerable luminescence quenching of CdSe-ZnS dots conjugated to SWNTs was reported due to FRET from dots to tubes [15]. This further suggests FRET to be dominant in bundles. This process is schematized in Figs. 5a,b for both one and two-photon spectroscopies.

In summary, we presented a thorough investigation of photoluminescence in nanotube bundles. We have shown that the apparently complex absorption and emission spectra can be simply explained by exciton energy transfer between adjacent semiconducting tubes. By studying the spectral evolution for increasing bundle size, we assigned all the excitation energy transfer peaks. We argue that Förster interaction between excitons dominates the transfer process. This is highly efficient in nanotube bundles, adding a major relaxation channel for excitons, explaining the low luminescence yield of large gap nanotubes. Thus, contrary to what usually assumed, bundles could be ideal for high yield optoelectronics applications, far surpassing the poor performance of individual tubes. Furthermore, energy transfer fingerprints bundles with different tube concentrations, finally offering a quantitative means to monitor the composition of solutions and films, a key requirement for research and applications.

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